



## Photocatalytic $\text{NH}_3$ versus $\text{H}_2$ evolution over $\text{g-C}_3\text{N}_4/\text{Cs}_x\text{WO}_3$ : $\text{O}_2$ and methanol tipping the scale

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### ABSTRACT

$\text{Cs}_x\text{WO}_3$  nanorods can be used to sensitize the single layer  $\text{g-C}_3\text{N}_4$ , where full spectrum light harvesting excited electrons to drive the photocatalytic reduction of  $\text{N}_2$  into  $\text{NH}_3$ . Under UV light, both water splitting and solar ammonia synthesis reaction exhibit high activity. However, selectivity towards ammonia over hydrogen is realized under NIR irradiation. With the control of methanol,  $\text{O}_2$  can directly decide the  $\text{NH}_3$  or  $\text{H}_2$  evolution on photocatalyst. The origin is the strong capture of  $\text{O}_2$  with the electrons from the photocatalyst under light irradiation to yield the oxygen active species, which transfer electrons subsequently with help of methanol to generate  $\text{NH}_3$ . However,  $\text{H}_2$  production will be suppressed by  $\text{O}_2$ . And with its sacrifice, methanol preserves the produced  $\text{NH}_3$  from oxidation. The  $\text{O}_2$ -sacrificial agent mediated  $\text{NH}_3$  evolution reaction found here provides insights in the promotion role of them in other catalysis.

### 1. Introduction

Solar driven nitrogen fixation has been considered to be a promising method to replace the traditional Haber-Bosch process, since the pioneering work reported by Schrauzer and Guth on the study of photocatalytic  $\text{N}_2$  fixation over titania based catalysts [1]. However, the wide band gap of titania based semiconductor, the poor interaction between catalyst and  $\text{N}_2$  molecules, and the high energy  $\text{N}_2$  intermediates make it difficult to perform photocatalytic  $\text{N}_2$  fixation [2]. Specially, the sufficient  $\text{N}_2$  activation, the prerequisite of its reduction, is crucial. The nitrogen fixation results are not satisfactory.

Recently, localized surface plasmon resonance (LSPR) of metallic nanostructures has received much attention because of its light-harvesting and electric-field-enhancing effects [3]. It reported that the conversion selectivity of  $\text{N}_2$  into  $\text{NH}_3$  could be improved through plasmon-induced charge separation over a  $\text{Au/Zr/SrTiO}_3$  catalyst [4]. In addition, efficient  $\text{N}_2$  photoreduction to  $\text{NH}_3$  has been achieved over oxygen vacancies introduced  $\text{BiOBr}$  nanosheets or nitrogen vacancies doped  $\text{g-C}_3\text{N}_4$  [5]. The research results indicated that the improved  $\text{N}_2$  photofixation abilities were benefited from enhanced  $\text{N}_2$  activation and promoted interfacial electron transfer. Then, other surface defects also show a similar effect on nitrogen photofixation, such as  $\text{Fe}^{3+}$  doping in  $\text{g-C}_3\text{N}_4$  and oxygen vacancies doped  $\text{BiOCl}$  [6].

It is known that  $\text{g-C}_3\text{N}_4$  has limitation to drive water oxidation and needs sacrificial electron donors such as alcohols [7]. The promotion of water oxidation will benefit providing sufficient  $\text{H}^+$  for  $\text{N}_2$  reduction, and then the efficiency of  $\text{NH}_3$  generation is improved [7]. Fortunately,  $\text{WO}_3$ -based semiconductors are considered to be good at water oxidation due to their proper band structure [8]. Therefore, due to the outstanding electron and proton conductivity, herein  $\text{g-C}_3\text{N}_4$  and  $\text{Cs}_x\text{WO}_3$  was selected to form a  $\text{g-C}_3\text{N}_4/\text{Cs}_x\text{WO}_3$  (CW) nanocomposite as the photoactive material to explore the  $\text{N}_2$  photofixation. Unique  $\text{N}_2$  reduction to ammonia was achieved by CW composite under NIR light irradiation. Careful studies evidently revealed the indispensable roles of  $\text{g-C}_3\text{N}_4$  and  $\text{Cs}_x\text{WO}_3$  in electron transfer and photo-induced protonation. Furthermore, by studying the LSPR assistance strategy, a possible mechanism of the nitrogen photofixation was proposed and the selectivity between hydrogen and ammonia generation was also discussed.

### 2. Experimental

All chemicals were purchased from Aladdin Chemical Reagent Co., Ltd. and used as received without further purification.

#### 2.1. Preparation of single layered $\text{g-C}_3\text{N}_4$

Single layer  $\text{g-C}_3\text{N}_4$  was prepared by the protonation treatment of

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bulk  $\text{g-C}_3\text{N}_4$  from the thermal polycondensation of melamine [9]. First, 1.60 g of melamine was heated at 550 °C for 3 h. Then, 1 g bulk one was dispersed in 5 ml HCl (37%) for 24 h. After centrifugation, washing and drying, the final single layer  $\text{g-C}_3\text{N}_4$  particles were obtained.

## 2.2. Preparation of $\text{Cs}_x\text{WO}_3$

Nanosized  $\text{Cs}_x\text{WO}_3$  was prepared by a solvothermal process [10].  $\text{WCl}_6$  ethanol solution and  $\text{CsOH}$  ethanol solution were mixed with a nominal Cs/W atomic ratio of 0.5 to form precursor solution. Then, after the solvothermal reaction, the final  $\text{Cs}_x\text{WO}_3$  was obtained after centrifugation, washing and drying.

## 2.3. Fabrication of $\text{g-C}_3\text{N}_4/\text{Cs}_x\text{WO}_3$ (CW) compounds

According to the differences in the surface electrical behaviour of protonated  $\text{g-C}_3\text{N}_4$  and  $\text{Cs}_x\text{WO}_3$ , it is easy to fabricate a uniform hybrid by electrostatic attraction in aqueous solution [11]. 0.5 g  $\text{Cs}_x\text{WO}_3$  and 2.0 g of as-prepared single layer  $\text{g-C}_3\text{N}_4$  were added into 100 ml of deionized water and then treated by ultrasonication for 4 h. The powder product was separated by centrifugation, and then vacuum dried at 60 °C overnight.

## 2.4. Characterization

X-ray diffraction (XRD) characterizations were performed on a Shimadzu XRD-6000 powder X-ray diffractometer with  $\text{CuK}\alpha$  radiation. The FT-IR spectra were recorded using a VERTEX 70 V/80V Fourier transformed infrared spectrometer (Bruker, Germany) by means of the KBr pellet technique. The UV/VIS diffuse reflectance spectra were obtained on a Perkin-Elmer Lambda 950 UV/VIS spectrometer equipped with Labsphere integrating over the spectral range of 250–1600 nm. Transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) images were obtained with a JEOL JEM-2100 microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurement was done using a Kratos AXIS Ultra DLD XPS system, all the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. The specific surface areas were measured out by the BET method (Micromeritics Instrumets, TriStar c3020). Electron spinning resonance (ESR) was measured by JES-FA300. Photocurrents were measured using an electrochemical analyzer (CHI 660b) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 1.00 cm × 1.00 cm, a Pt sheet and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. A 0.1 M  $\text{Na}_2\text{SO}_4$  solution was used as the electrolyte. Ar and  $\text{N}_2$  were introduced into reactor respectively. The electrochemical impedance spectroscopy (EIS) was measured at –1.4 V (vs. RHE) in 0.5 M  $\text{Na}_2\text{SO}_4$  solution, and the perturbation signal was 5 mV with the frequency ranged from 0.1 Hz to 100 kHz. Atomic force microscopy (AFM) analysis was performed by Agilent 5500 ILM. A Vario EL cube was employed to carry out elementary analysis and an IRIS ER/S was used to determine element content via inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Optical spectra of the  $\text{Cs}_x\text{WO}_3$  were measured in tetrachloroethylene (TCE), dimethylformamide (DMF), and acetonitrile (MeCN) solution on a Perkin-Elmer Lambda 950 UV/VIS spectrometer equipped with Labsphere integrating over the spectral range of 250–1600 nm.

Determination of  $\text{NH}_4^+$  cations by ion chromatography (IC) method was achieved by using a Dionex ICS-1500 ion chromatograph (Dionex, Sunnyvale, CA, USA). The chromatographic system consisted of an advanced gradient pump and a DS-6 conductivity detector. Chromatographic separations on a Dionex IonPac®-CS12 cation exchanger was performed using a cation Self Regenerating Suppressors (CERS 4 mm) with a flow rate of 1.0 ml/min. The injection volume was 25  $\mu\text{l}$  for each sample. Rotary evaporation operation was conducted to remove methanol from the reaction solution.

## 2.5. LC-MS analysis

Indophenol method based on the LC-MS was used to determine the quantitative of  $\text{NH}_3$  generation [6]. The reaction solution was injected directly for analysis. All the products were investigated in ESI (positive ion mode) on an Ultimate 3000-TSQ (LCMS-ESI).

## 2.6. Photocatalytic $\text{N}_2$ fixation

Typically, 20 mg of sample was dispersed in an aqueous solution (40 ml) containing 10 vol. % methanol as an electron donor. 3 wt% platinum was used as a cocatalyst. Prior to irradiation, the reaction solution was sealed by a silicone stopper, and subsequently flushed with dry  $\text{N}_2$  in both of solution and atmosphere to remove  $\text{O}_2$  completely. In comparison, the experiments were also carried out with dissolving  $\text{O}_2$  in solution or air condition.  $\text{NH}_3$  yield was determined via a colorimetric method using Nessler reagent as an indicator [5]. Typically, 1.5 ml reaction solution was added to 1 ml of KOH (0.25 M) and then mixed thoroughly with 0.25 ml 0.2 M  $\text{KNaC}_4\text{H}_4\text{O}_6$  and 0.25 ml Nessler reagent. The mixed solution incubated for 20 min at room temperature. The absorbance of the solution at 425 nm was measured by the UV/VIS spectrometer. The calibration curves are shown in Fig. S9a.

The active species generated in the photocatalytic  $\text{N}_2$  fixation process could be detected through trapping by 5.0 mg of  $\text{AgNO}_3$ , isopropyl alcohol (IPA), ammonium oxalate (AO) or benzoquinone (BQ).

## 2.7. Photocatalytic $\text{H}_2$ or $\text{O}_2$ evolution

To determine the evolved hydrogen or oxygen, a calibrated Varian GC-3380 Gas Chromatograph equipped with a thermal conductivity detector was employed using Ar as the carrier gas as our previous work [9]. Hydrogen production was carried out by dispersing 50 mg of as-prepared sample in an aqueous solution (100 ml) containing 10 ml of the 10 vol % sacrificial agent as an electron donor. 3 wt% platinum was used as a cocatalyst. Oxygen production was performed by dispersing the same amount of sample but in an aqueous  $\text{AgNO}_3$  solution (0.01 M, 100 ml). For pure water splitting, 3 wt% platinum was used as a cocatalyst and 0.005 M of NaI was added as a redox mediator.

## 2.8. Photoelectrochemical $\text{N}_2$ fixation

All the electrodes and experimental conditions are the same as the photocurrent measurement, except for inducing 10 vol. % methanol as a electron donor in the sealed chamber. Before irradiation,  $\text{N}_2$  was introduced into reactor for 20 min. The  $\text{NH}_3$  and  $\text{H}_2$  yields were detected as the same methods above.

## 2.9. Light source

- a full spectrum LED lamp (365–940 nm) with the intensity of 100 mW/cm<sup>2</sup>;
- a series of monochromatic LED lamp (365, 395, 405, 425, 850, 940 nm) with the same intensity of 20 mW/cm<sup>2</sup>.

## 2.10. Theoretical Calculation

All the calculations for pristine  $\text{g-C}_3\text{N}_4$  and V-rich  $\text{g-C}_3\text{N}_4$  were carried out using density functional theory (DFT) calculations with  $\omega\text{B97X-D}/6-31\text{G}(\text{D})^*$  basis setting for both geometry optimization and frequency calculation on Gaussian09 program. The  $\omega\text{B97X-D}$  functional is a long range dispersion-corrected functional and is good for non-covalent interactions [28]. Energies of respective surface bound intermediates and free molecules are corrected by the corresponding zero-point energy. For more details, please see the data in Table S5.

### 2.11. Apparent quantum yield calculations

The apparent quantum yield (AQY) for the NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> evolution was determined under 20 mW/cm<sup>2</sup> monochromatic light irradiation. The AQY was calculated as:

$$\text{AQY} = \frac{N_e}{N_p} \times 100\% = \frac{NMN_A hc}{SPt\lambda} \times 100\%$$

where  $N_e$  is the amount of reaction electrons,  $N_p$  is the amount of incident photons,  $N_A$  is Avogadro's constant,  $h$  is the Planck constant,  $c$  is the speed of light,  $S$  is the irradiation area,  $P$  is the intensity of the irradiation,  $t$  is the irradiation time, and  $\lambda$  is the wavelength of the monochromatic light. For the AQY of H<sub>2</sub>, NH<sub>3</sub> and O<sub>2</sub>, the NM represent for 2 M(H<sub>2</sub>), 3 M(NH<sub>3</sub>) and 4 M(O<sub>2</sub>) [6].

## 3. Results and discussion

For the first time, a uniform hybrids of g-C<sub>3</sub>N<sub>4</sub> and Cs<sub>x</sub>WO<sub>3</sub> was obtained by electrostatic attraction in aqueous solution. Single layer g-C<sub>3</sub>N<sub>4</sub> nanosheets with abundant N vacancies and O dangling bonds were exfoliated by protonation [9]. Oxygen vacancies rich Cs<sub>x</sub>WO<sub>3</sub> nanorods were synthesized through hydrothermal method [10]. CW composites were fabricated by self assembly, owing to the opposite surface electrochemical properties [11]. As shown in the TEM image (Fig. S1a1-3), Cs<sub>x</sub>WO<sub>3</sub> nanorods are dispersed on the surface of single layer g-C<sub>3</sub>N<sub>4</sub> nanosheets. AFM measurement confirms that the thickness of the single nano-layer g-C<sub>3</sub>N<sub>4</sub> under study is about 0.5 nm (in Fig. S1b1-3). The use of single nano-layer g-C<sub>3</sub>N<sub>4</sub> is convenient to improve the separation of electron-hole pairs in it. It is known that the SPR is sensitive to the refractive index (RI) of solvent and there is a linear relationship between the solvent RI and the plasmon peak position [12]. The optical spectra of Cs<sub>x</sub>WO<sub>3</sub> were collected in tetrachloroethylene (TCE), dimethylformamide (DMF), and acetonitrile (MeCN), with respective RIs of 1.51, 1.43, and 1.35. There is an obvious and systematic shift of the peak position to a longer wavelength with the solvent RI increases (Fig. S1c). The results from the insert plot of RI versus peak wavelength further indicates the plasmon resonance absorption [13].

As indicated by XRD pattern (Fig. S2a), the characteristic peaks belonged to the hexagonal phase of cesium tungsten bronze (JCPDS No. 831334) are all presented in the XRD pattern of CW composite without any impurity peak. The (002) peak of g-C<sub>3</sub>N<sub>4</sub> should be overlapped by the peak at ~27.4° of Cs<sub>x</sub>WO<sub>3</sub>. FT-IR spectra show no extra impurity peak between pure g-C<sub>3</sub>N<sub>4</sub> or Cs<sub>x</sub>WO<sub>3</sub> and CW composite (Fig. S2b). The peaks at 674 and 972 cm<sup>-1</sup> can be ascribed to the W–O–W and W=O bonds respectively, suggesting the presence of W metal with different valence [14]. XPS was further used to investigate the chemical composition of CW sample (Fig. S3). O 1s spectra (Fig. S3a) of all samples exhibit two same peaks, one at ca. 532.7 eV caused by the adsorbed H<sub>2</sub>O and another one at ca. 531.7 eV attributed to the surface hydroxyl group [15]. One additional peak for CW and Cs<sub>x</sub>WO<sub>3</sub> at ca. 530.2 eV can be ascribed to the W–O bond [16]. CW composite shows a stronger peak at 531.7 eV and a weaker peak at 532.7 eV similar to those in g-C<sub>3</sub>N<sub>4</sub>, while the 532.7 eV peak is stronger than the 531.7 eV peak in Cs<sub>x</sub>WO<sub>3</sub>. The increase of hydroxyl group is originated from g-C<sub>3</sub>N<sub>4</sub> constituent, confirming that CW has been fabricated instead of simple mixture.

Since vacancies may play an important role in photocatalytic N<sub>2</sub> reduction process [6], besides XPS, ESR analysis was also performed (Figs. S3 and S4). The peaks at 287.8 and 288.2 eV are ascribed to C–N<sub>2</sub> and C–N<sub>3</sub> in C1s spectra (Fig. S3b). C–N<sub>2</sub> peak is much weaker and C–N<sub>3</sub> peak even disappears after protonation, indicating the planar destruction. In N 1s spectra (Fig. S3c), C–N–C peak becomes much weaker and N–C<sub>3</sub> peak also disappears after protonation, suggesting N lost in tri-s-triazine rings. The sharp peak with  $g = 2.0034$  also confirms the

vacancies in the protonated g-C<sub>3</sub>N<sub>4</sub> (Fig. S4) [17]. In W 4f spectra (Fig. S3d), Cs<sub>x</sub>WO<sub>3</sub> and CW show W<sup>5+</sup> and W<sup>6+</sup> peaks, owing to oxygen vacancies [11]. The partial oxidation of CN after protonation results in O adsorption and O dangling bonds on the surface of g-C<sub>3</sub>N<sub>4</sub> [9]. Replacing N with O promotes the positive electricity of C, benefiting the N<sub>2</sub> adsorption and the N–N triple bond weakening [18]. Furthermore, the protonation brings hydroxyl and carboxyl to the surface of catalysts. The hydroxyl or carboxyl could act as a proton donor in the reaction and then greatly improves the N<sub>2</sub> conversion efficiency [19].

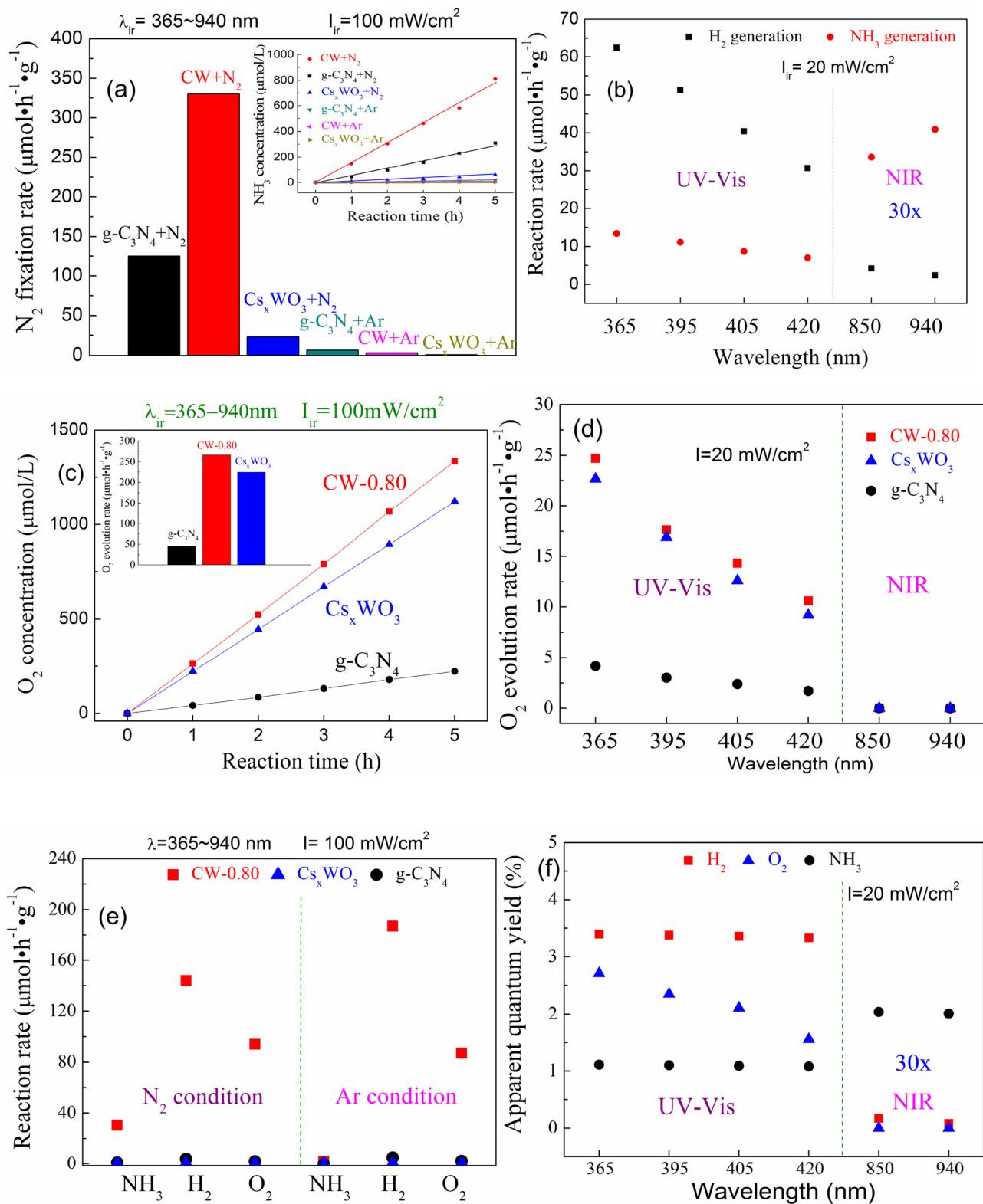
DRS spectra were measured to evaluate the optical absorption ability of as-prepared samples (Fig. S5a). CW shows a wide range of light absorption from UV, Vis to the whole NIR region, indicating its potential in full-spectrum light driven catalytic reaction. The band gaps are estimated from the tangent lines in the plots of the square root of the Kubelka-Munk functions against the photon energy [20]. The result (Table S1) shows that the band gap energy increases from 2.88 to 2.92 then to 3.21 eV with increasing the Cs<sub>x</sub>WO<sub>3</sub> content from g-C<sub>3</sub>N<sub>4</sub> to CW then to Cs<sub>x</sub>WO<sub>3</sub>. Ultraviolet photoelectron spectra (UPS) were then carried out to determine the relative valence band maximum (Fig. S5b). The valence band edges of g-C<sub>3</sub>N<sub>4</sub>, CW and Cs<sub>x</sub>WO<sub>3</sub> are 2.21, 2.46 and 2.98 eV. Thus, the calculated conduction band edges are -0.67, -0.46 and -0.23 eV. Their specific surface area values are almost the same as ca. 35 m<sup>2</sup>/g (Table S1), indicating that surface area should not be the key factor.

Initial studies on the photocatalytic activity for N<sub>2</sub> fixation over as-prepared samples were carried out by irradiating with a full-spectrum lamp, using water as the reactant and proton source and 10% methanol as the electron donor. As shown in Fig. 1a, a large amount of NH<sub>3</sub> (813 μmol L<sup>-1</sup>) can be generated over CW in N<sub>2</sub> atmosphere, while the NH<sub>3</sub> yields of g-C<sub>3</sub>N<sub>4</sub> and Cs<sub>x</sub>WO<sub>3</sub> are 304 and 63 μmol L<sup>-1</sup> after 5 h, respectively. The full-spectrum light induced NH<sub>3</sub> generation rate is estimated to be 331 μmol h<sup>-1</sup> per one gram of catalyst of CW, 2.6 and 14.4 times higher than g-C<sub>3</sub>N<sub>4</sub> and Cs<sub>x</sub>WO<sub>3</sub> (125 and 23 μmol h<sup>-1</sup> g<sup>-1</sup>). After cycling test, no significant photoreactivity decrease is observed, indicating the photo-stability of CW for ammonia synthesis (Fig. S6a).

H<sub>2</sub> and NH<sub>3</sub> generation selectivity is also investigated. As shown in Fig. S6b, under full-spectrum light irradiation, the H<sub>2</sub> evolution rates of g-C<sub>3</sub>N<sub>4</sub>, Cs<sub>x</sub>WO<sub>3</sub> and CW are 831, 83 and 1544 μmol h<sup>-1</sup> g<sup>-1</sup>, which are 6.6, 3.6 and 4.7 times higher than their own NH<sub>3</sub> generation rate, respectively, suggesting that all samples exhibit a low overpotential for hydrogen evolution and a high overpotential for nitrogen reduction [21]. Besides the poor proton affinity of N<sub>2</sub>, the N<sub>2</sub> reduction requires quite high reaction energy. The dissociation of N<sub>2</sub> triple bond needs the energy as high as 944 kJ/mol [22]. The conversion of N<sub>2</sub> to N<sub>2</sub>H requires a large energy of 313.8 kJ/mol [6]. However, the splitting of H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub> needs only 237.2 kJ/mol [23]. Therefore, water splitting proceeds more easily than N<sub>2</sub> reduction.

To further study the selectivity over CW, the monochromatic light driven experiments were carried out (Fig. 1b, Table S2). Under UV light irradiation, it displays good activity in both NH<sub>3</sub> and H<sub>2</sub> generation. H<sub>2</sub> evolution rate is ca. 4 times higher than that of NH<sub>3</sub>, indicating that UV light benefits for water splitting. However, N<sub>2</sub> reduction could be greatly promoted under NIR irradiation, since NH<sub>3</sub> generation rates are 1.1 μmol h<sup>-1</sup> g<sup>-1</sup> (850 nm) and 1.4 μmol h<sup>-1</sup> g<sup>-1</sup> (940 nm), 8 and 17 times higher than that of H<sub>2</sub>. According to the material property, a plenty of excited electrons are generated in CW by UV light, while the NIR induced LSPR effect can only provide energy for limited hot electron and hole separation in Cs<sub>x</sub>WO<sub>3</sub> component [24].

Water oxidation was also carried out in the 0.01 M AgNO<sub>3</sub> solution under UV-vis-NIR or monochromatic light source. Fig. 1c shows the oxygen production results over g-C<sub>3</sub>N<sub>4</sub>, Cs<sub>x</sub>WO<sub>3</sub> and CW. Under full-spectrum light irradiation, the O<sub>2</sub> evolution rates of g-C<sub>3</sub>N<sub>4</sub>, Cs<sub>x</sub>WO<sub>3</sub> and CW are 44.6, 224.6 and 266.5 μmol h<sup>-1</sup> g<sup>-1</sup> respectively. It is clear that after coupling Cs<sub>x</sub>WO<sub>3</sub>, CW exhibits excellent O<sub>2</sub> evolution activity 6 times higher than g-C<sub>3</sub>N<sub>4</sub>. Then, the water oxidation activity was also investigated under monochromatic light irradiation. As shown in



**Fig. 1.** (a)  $\text{NH}_3$  production over  $\text{Cs}_x\text{WO}_3$ ,  $\text{g-C}_3\text{N}_4$  and CW under full spectrum light irradiation in  $\text{N}_2/\text{Ar}$  gas under  $\text{O}_2$ -free condition with 10% methanol. (b)  $\text{NH}_3$  and  $\text{H}_2$  generation rates over CW under UV or NIR monochromatic light under  $\text{O}_2$ -free condition with 10% methanol. (c)  $\text{O}_2$  production over  $\text{g-C}_3\text{N}_4$ ,  $\text{Cs}_x\text{WO}_3$  and CW under UV–vis–NIR light irradiation. (d)  $\text{O}_2$  generation rates over  $\text{g-C}_3\text{N}_4$ ,  $\text{Cs}_x\text{WO}_3$  and CW under monochromatic light irradiation. (e)  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{O}_2$  generation rates over different samples with 3 wt% platinum in a 0.005 M NaI solution with  $\text{N}_2$  or Ar under full spectrum light irradiation. (f) Apparent quantum yields of  $\text{H}_2$ ,  $\text{NH}_3$  and  $\text{O}_2$  under different monochromatic light irradiation.

**Fig. 1d**, CW exhibits much higher O<sub>2</sub> evolution efficiency than g-C<sub>3</sub>N<sub>4</sub> under UV light irradiation. However, no O<sub>2</sub> evolution was observed under NIR light irradiation, suggesting the lack of holes to drive water oxidation reaction.

Since CW is good at N<sub>2</sub> reduction and water oxidation, the photocatalytic NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> generations in the pure water were further performed. The 3 wt% platinum was used as a cocatalyst and 0.005 M NaI was added as a redox mediator [25]. As shown in **Fig. 1e**, only CW shows high NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> evolution rates under full-spectrum irradiation in N<sub>2</sub> atmosphere, the NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> generation rates are 30.4, 144.1 and 94.2 μmol h<sup>-1</sup> g<sup>-1</sup> respectively, indicating that the CW would act well in both reduction and oxidation reaction. However, in Ar atmosphere, the NH<sub>3</sub> or O<sub>2</sub> production decreased while the H<sub>2</sub> generation increased. The generation rates of NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> are 0, 186.9 and 86.9 μmol h<sup>-1</sup> g<sup>-1</sup>. The generation ratio of H<sub>2</sub> to O<sub>2</sub> is ca. 2, also confirming the good pure water splitting activity of CW. In addition, no NH<sub>3</sub> generation in Ar atmosphere strongly confirms the crucial role of N<sub>2</sub> gas in NH<sub>3</sub> production.

Therefore, in **Fig. 1f** and Table S3, the apparent quantum yield (AQY) of the photocatalytic hydrogen evolution system over CW was determined to be 3.40, 3.38, 3.36 and 3.33% at 365, 395, 405 and 420 nm respectively. But, the AQY was quite low in NIR light region. Similar to H<sub>2</sub> generation, N<sub>2</sub> fixation exhibits the same AQY values under different UV light irradiation. The AQY of ammonia generation was 1.11, 1.10, 1.09, 1.08% at 365, 395, 405 and 420 nm. The AQY of ammonia generation is lower than that of hydrogen evolution, suggesting that UV light is positive for hydrogen evolution. However, the AQY of NIR light induced NH<sub>3</sub> generation was quite high. The AQY of ammonia generation were 0.068 (850 nm) and 0.067% (940 nm), 12 and 25 times higher than that of H<sub>2</sub> evolution under the same NIR light irradiation. Different from that of hydrogen or ammonia generation, the AQY value of O<sub>2</sub> evolution obviously decrease with the wavelength of light source increase in UV region. The AQY of O<sub>2</sub> evolution is 2.71, 2.35, 2.11 and 1.56% at 365, 395, 405 and 420 nm. No photocatalytic oxygen evolution was observed under NIR light irradiation. It is worth mentioning that the N<sub>2</sub> reduction was carried out under 365–940 nm light irradiation without additional sacrificial reagent or H<sub>2</sub> input. The as-prepared CW composite shows higher N<sub>2</sub> fixation ability than many other g-C<sub>3</sub>N<sub>4</sub> or graphene based composite photocatalyst, as shown in Table S4.

It is well known that the photocatalytic water splitting for hydrogen evolution is achieved by photogenerated charge carriers [23]. It is easy for O<sub>2</sub> to capture electrons to form ·O<sub>2</sub><sup>-</sup>, resulting in the H<sub>2</sub> generation decrease [23]. Therefore, for a large yield of H<sub>2</sub>, O<sub>2</sub> is usually removed completely before the water splitting reaction takes place. On the other hand, electron transfer also plays an important role in the photocatalytic N<sub>2</sub> fixation. With the electron participation, both oxidation and reduction reactions can realize the N<sub>2</sub> fixation [1]. Since O<sub>2</sub> is a excellent electron acceptor, the performances of O<sub>2</sub> and its related free radicals should not be ignored.

To investigate the effect of O<sub>2</sub>, the measurements of hydrogen and ammonia synthesis were carried out with different O<sub>2</sub> condition in a sealed chamber. As shown in **Fig. 2a**, with the O<sub>2</sub> content increase, there is a sharp decline in production of hydrogen. However, the yield of NH<sub>3</sub> is enhanced instead under the same condition. It suggests that O<sub>2</sub> plays a positive role in NH<sub>3</sub> formation. The influence of O<sub>2</sub> will further discussed after the study of the hole scavenger.

The presence of organic scavengers such as methanol will benefit for ammonia generation. It could obviously increase the NH<sub>3</sub> yield by means of methanol as an electron donor in the semiconductor [26]. In addition, methanol is also a superior ·OH scavenger. With its sacrifice, methanol protects the produced NH<sub>3</sub> from further oxidation [26]. As shown in **Fig. 2b**, after adding methanol, a dramatic enhancement of nitrogen conversion rate can be observed, owing to the reduced charge combination. The system with 10% methanol addition could generate the largest amount of NH<sub>3</sub>. But the further increase addition of

methanol will cause an excessive expenditure of active species, resulting in a fewer NH<sub>3</sub> product. Adding 10% ethanol, the similar enhancement is achieved, though not as highly as methanol plays.

After going on to add different scavengers to the 10% methanol-reaction system, different N<sub>2</sub> fixation rates will be achieved. As shown in **Fig. 3a**, the ·O<sub>2</sub><sup>-</sup> scavenger (BQ) and ·OH scavenger (IPA) will bring a damage to the ammonia yield, suggesting the oxygen active species play an important role in the N<sub>2</sub> conversion. Then, a more serious declination is observed in the N<sub>2</sub> fixation rate, after adding another electron scavenger, AgNO<sub>3</sub>. The sharp decrease caused by AgNO<sub>3</sub> indicates that electrons are crucial in the N<sub>2</sub> fixation. Compared with the results under the condition of oxygen dissolved in the solution, the absence of O<sub>2</sub> will results in a lower N<sub>2</sub> fixation rate, confirming O<sub>2</sub> and its active species play a positive role in the ammonia generation.

The effect of electron and O<sub>2</sub> on the hydrogen and ammonia generation was also studied under a LED light irradiation with the wavelength of 365 or 940 nm. As shown in **Fig. 3b**, the lack of electrons is a horror for both hydrogen and ammonia synthesis, since AgNO<sub>3</sub> has been added. The ·O<sub>2</sub><sup>-</sup> and ·OH scavengers will also reduce the generation rate. However, the presence of O<sub>2</sub> plays an entirely different role between H<sub>2</sub> and NH<sub>3</sub> evolution, which decreases the H<sub>2</sub> yield but improves the NH<sub>3</sub> generation. According to the above results, O<sub>2</sub> can improve the N<sub>2</sub> conversion, but it will injure the H<sub>2</sub> evolution seriously.

To elucidate the role of holes and O<sub>2</sub> in the catalytic reaction, the evaluation of ammonia and hydrogen generation rate was also carried out under different condition using a monochrome LED light. As shown in **Fig. 4**, after adding the hole scavenger methanol, the yields of both NH<sub>3</sub> and H<sub>2</sub> under different O<sub>2</sub> condition are greatly improved. Without the electron donor methanol, the yield of NH<sub>3</sub> or H<sub>2</sub> decreases with the O<sub>2</sub> content increase, owing to the electron expenditure. The ·O<sub>2</sub><sup>-</sup> and ·OH may oxidize NH<sub>3</sub> in the absence of sacrificial agent methanol. But, with the assistance of methanol, O<sub>2</sub> active species will release the electrons for catalytic reaction. The positive effect of O<sub>2</sub> active species under the methanol control has been confirmed in the above analysis (**Fig. 3**).

Under UV light (365 nm) irradiation, the presence of both O<sub>2</sub> and methanol shows a positive role in the enhancement of NH<sub>3</sub> generation, while O<sub>2</sub> harms the H<sub>2</sub> evolution seriously (**Fig. 4a–b**). For NH<sub>3</sub> synthesis, methanol has a much stronger influence than O<sub>2</sub>. But the addition 20% methanol will cause an excessive expenditure of active species, resulting in a fewer NH<sub>3</sub> product than that of 10% methanol. However, under NIR light (940 nm) irradiation, the limited hot electrons and holes will be induced by LSPR effect only in Cs<sub>x</sub>WO<sub>3</sub> component. The effect of methanol and O<sub>2</sub> on the N<sub>2</sub> conversion under NIR light is the same as that under UV light (**Fig. 4c**). For H<sub>2</sub> evolution, both the positive role of methanol and the negative role of O<sub>2</sub> are amplified (**Fig. 4d**). It is clear that the removal of O<sub>2</sub> will benefit for H<sub>2</sub> evolution, though the electrons are not enough. Therefore, the results indicate that without methanol, O<sub>2</sub> harms both hydrogen and ammonia evolution, while O<sub>2</sub> becomes a friend to the N<sub>2</sub> conversion with the assistance of methanol.

To further investigate the effect of O<sub>2</sub>, the indophenol created in the reaction between NH<sub>4</sub><sup>+</sup> and phenolic-hypochlorite in different O<sub>2</sub> condition with the same 10% methanol under full-spectrum light irradiation was analyzed by LC-MS. As shown in **Fig. 5a**, a strong indophenol anion mass spectroscopy signal presents at 198 m/z, while a weak signal at 199 m/z also appears. The 199 m/z signal can be ascribed to the existence of <sup>15</sup>N<sub>2</sub> in the atmosphere. It is clear that a much stronger signal can be observed with the existence of O<sub>2</sub>, indicating again that O<sub>2</sub> plays an active role in the N<sub>2</sub> fixation.

The products created from N<sub>2</sub> fixation under different O<sub>2</sub> condition with the same 10% methanol was also analyzed by LC-MS. As shown in **Fig. 5b**, obviously, four peaks corresponding to the ion mass of [HCHO + H]<sup>+</sup>, [NH<sub>2</sub>OH + H]<sup>+</sup>, [CH<sub>3</sub>OCH<sub>3</sub> + H]<sup>+</sup> and [NH<sub>2</sub>NH<sub>2</sub> + H]<sup>+</sup> can be observed. The former three are the ·OH induced reaction products, while the last one generated from the electron reduction procedure. HCHO and CH<sub>3</sub>OCH<sub>3</sub>

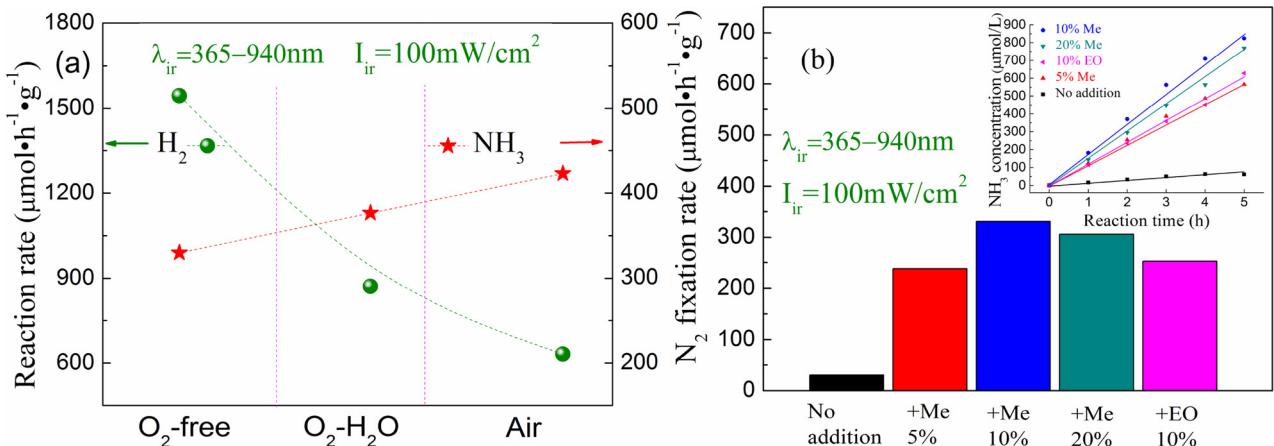


Fig. 2. (a)  $\text{NH}_3$  and  $\text{H}_2$  generation over CW photocatalyst under full spectrum light irradiation in 10% Me aqueous solution with different  $\text{O}_2$  condition; (b)  $\text{NH}_3$  production over CW composite with adding a different volume content of methanol or ethanol under  $\text{O}_2\text{-H}_2\text{O}$  condition. (Me: methanol, EO: ethanol).

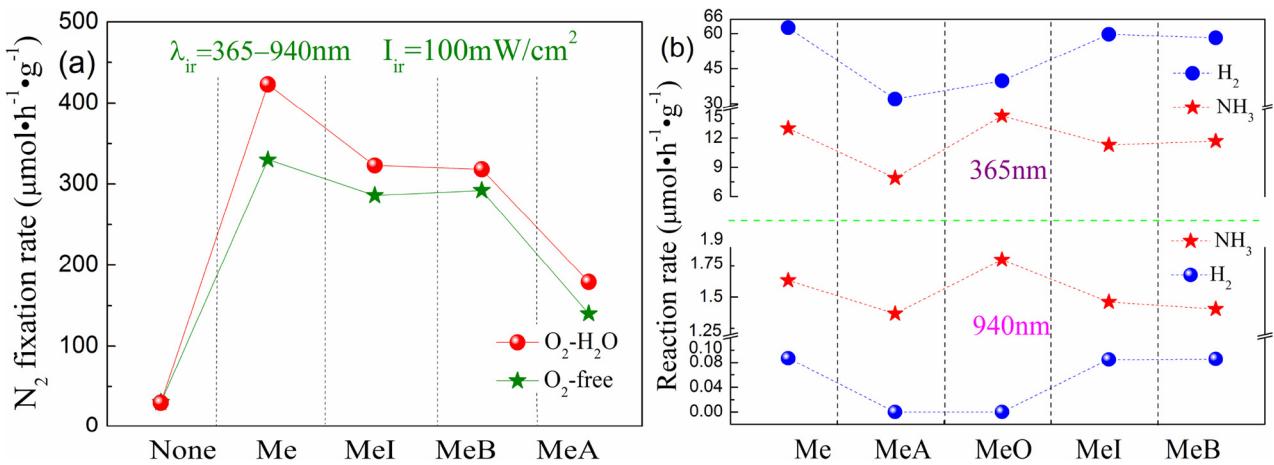


Fig. 3. (a)  $\text{NH}_3$  production over CW under  $\text{O}_2$ -free or dissolved  $\text{O}_2$  condition with different addition; (b)  $\text{NH}_3$  and  $\text{H}_2$  production over CW composite under UV or NIR monochromatic light with different addition. (Me: methanol, MeA: Me +  $\text{AgNO}_3$ , MeI: Me + IPA, MeB: Me + BQ, MeO: Me +  $\text{O}_2\text{-H}_2\text{O}$ ).

come from the oxidation of methanol, while  $\text{NH}_2\text{OH}$  can be attributed to the combination reaction of  $\cdot\text{OH}$  with  $\cdot\text{NH}_2$  formed in nitrogen reduction process [26]. The signals of  $\text{HCHO}$ ,  $\text{NH}_2\text{OH}$  and  $\text{CH}_3\text{OCH}_3$  become stronger in the presence of  $\text{O}_2$ . No nitrite or nitrate signal appears, but the oxidation of methanol can be confirmed. It infers that the produced ammonia do not be oxidized with the presence of methanol. Therefore, it confirms that both  $\text{O}_2$  and methanol play a key role in  $\text{N}_2$  fixation.

Ion chromatography (IC) was also employed to determine the  $\text{NH}_4^+$  concentration in the reaction solution. A 0.25 mM  $\text{NH}_4\text{Cl}$  solution was used as the standard. As shown in Fig. 5c, two peaks at 3.74 and 4.19 min can be observed, owing to the  $\text{Na}^+$  from water and  $\text{NH}_4^+$  respectively [27]. All the samples exhibit the signal peak at 3.74 min, which can be ascribed to the  $\text{Na}^+$  containing in the pure water. However, no peak was observed at 4.19 min in the pure water or the dark reaction solution, indicating that the light irradiation was crucial in the  $\text{NH}_4^+$  generation. Then, the reaction solution for CW,  $\text{Cs}_x\text{WO}_3$  or  $\text{g-C}_3\text{N}_4$  samples under 20 h full-spectrum light irradiation was analyzed. According to the calibration curve for  $\text{NH}_4^+$  concentration using IC method (shown in Fig. S9b), the  $\text{NH}_4^+$  production rate for CW is  $137.7\text{ }\mu\text{mol h}^{-1}\text{ g}^{-1}$ , 3.0 and 11.3 times higher than that of  $\text{g-C}_3\text{N}_4$  and  $\text{Cs}_x\text{WO}_3$  ( $45.8$  and  $12.2\text{ }\mu\text{mol h}^{-1}\text{ g}^{-1}$ ), which is similar to the results in Nessler colorimetric method.  $\text{NH}_4^+$  production for CW samples under 200 h NIR or UV monochromatic LED light irradiation was also investigated (in Fig. 5d).  $\text{NH}_4^+$  productions under NIR and UV are 0.51 and  $5.4\text{ }\mu\text{mol h}^{-1}\text{ g}^{-1}$  respectively, while the  $\text{NH}_4^+$  generation for CW sample in the pure water under 20 h full-spectrum light irradiation is

$16.1\text{ }\mu\text{mol h}^{-1}\text{ g}^{-1}$ . The calculated  $\text{NH}_3$  yield in IC and Nessler colorimetric method are listed in Table S5. Though the  $\text{NH}_3$  yields in IC characterization are lower than those by using Nessler reagent, the relative  $\text{NH}_3$  generation rates among different samples are the same between IC and Nessler reagent results.

To further investigate the products during  $\text{N}_2$  fixation, maleic acid or extra  $\text{N}_2\text{H}_4$  was added to the reaction solution (Fig. S6c, Table S6). Under light irradiation,  $\text{N}_2$  reduction over CW is suppressed after adding the  $\text{N}_2\text{H}_2$  scavenger maleic acid, indicating that  $\text{N}_2\text{H}_2$  is an important intermediate. But the addition of oxalic acid without a C=C bond slightly suppressed the  $\text{N}_2$  fixation efficiency of CW. Instead, an obvious enhancement of  $\text{NH}_3$  generation is observed under both UV and NIR light irradiation after adding extra  $\text{N}_2\text{H}_4$ . Compared to the average growth rate of 2.5 times under UV light, a notable increase of  $\text{NH}_3$  generation (9.7 times) is obtained under NIR irradiation. If any intermediate amount decreases or increases, the  $\text{NH}_3$  yield will decrease or increase. More measurements were carried out under different temperature without light irradiation. As listed in Table S7, in the dark condition, with temperature rise, no  $\text{NH}_3$  product was obtained, suggesting the importance of light irradiation. In addition, in the Ar atmosphere, all the photocatalysts including  $\text{g-C}_3\text{N}_4$  show poor activities on  $\text{N}_2$  conversion, even if under full-spectrum light irradiation (Fig. 1a). The slight amount of  $\text{NH}_3$  may come from  $\text{N}_2$  residues in Ar atmosphere. It confirms again that all the photocatalysts are stable during  $\text{N}_2$  fixation. The  $\text{NH}_3$  yields are 13.4 and  $1.6\text{ }\mu\text{mol/g h}$  under 365 and 940 nm respectively. Interestingly, using these two monochrome LED lamp

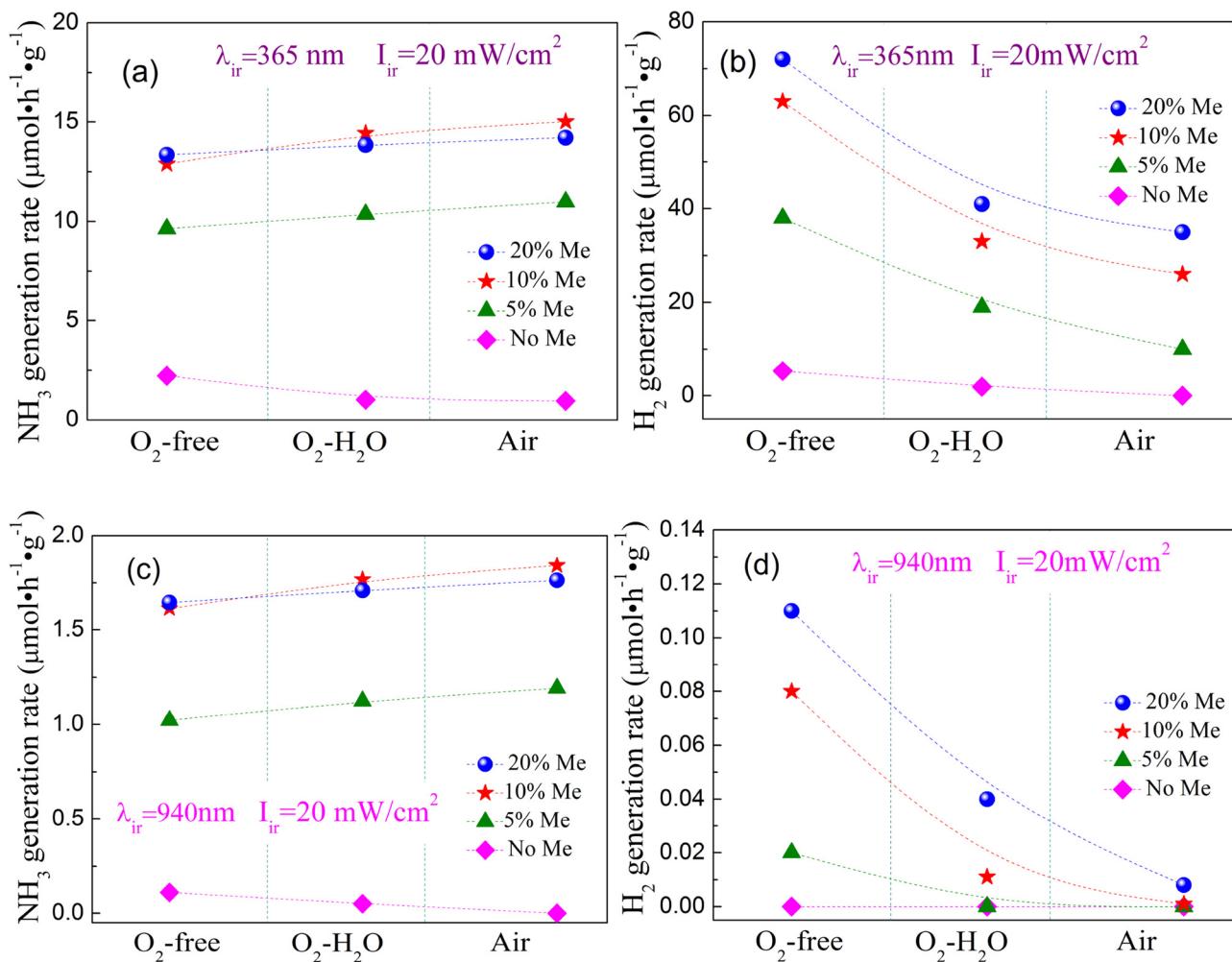


Fig. 4. (a,c) NH<sub>3</sub> and (b,d) H<sub>2</sub> production over CW composite under UV (365 nm) or NIR (940 nm) monochromatic light with different methanol.

simultaneously as the light source, 18  $\mu\text{mol/g h}$  of NH<sub>3</sub> generation can be realized. The mixed light driven activity is improved greatly, 1.2 times higher than the result by adding up the UV and NIR induced activity values, indicating that a synergy effect is achieved. The LSPR effect can also provide extra excited state and active site [24]. Excited electrons can utilize the extra advantages and then efficiently activate N<sub>2</sub> fixation.

As indicated in Fig. 6a, the photocurrent response was tested in different atmosphere. In Ar gas, the photocurrent for CW reaches up to 3.0  $\mu\text{A/cm}^2$ , while 1.0  $\mu\text{A/cm}^2$  in N<sub>2</sub> saturated atmosphere, suggesting that the photoelectron can be absorbed by N<sub>2</sub> [28]. EIS results also confirm that CW exhibits excellent charge transfer ability (Fig. S7). Then, photoelectrochemical (PEC) experiments over CW were performed under 365 or 940 nm light (Fig. 6b). All the yields increase with the time being and the UV H<sub>2</sub> evolution and NIR NH<sub>3</sub> generation show sharper rise. After 15 h, the yields of H<sub>2</sub> are 2535.0 nmol (365 nm) and 17.0 nmol (940 nm), while that of NH<sub>3</sub> are 279.0 nmol (365 nm) and 121.5 nmol (940 nm), respectively. The PEC NH<sub>3</sub> generation rates are 18.6 nmol/h (365 nm) and 8.1 nmol/h (940 nm), while the H<sub>2</sub> evolution rates are 169.0 nmol/h (365 nm) and 1.1 nmol/h (940 nm), respectively. H<sub>2</sub> evolution rates are 9.1 and 0.1 times higher than NH<sub>3</sub> generation rates under UV and NIR light irradiation. Compared with that using UV light, the efficiency of NIR induced PEC NH<sub>3</sub> generation has been improved greatly, owing to the limitation of LSPR by which only N<sub>2</sub> fixation reaction can be improved, similar to the result in the above photocatalytic reaction. The photoelectrochemical results also indicate the importance of electron.

Then, DFT method with  $\omega$ B97X-D/6-31G(D)\* basis set was carried out to optimize the geometry and frequency of vacancy-rich (V-rich) and pristine g-C<sub>3</sub>N<sub>4</sub> (Fig. 7a and S8). Three zones are chosen as potential active sites waiting for N<sub>2</sub> molecule insertion. As indicated in Table S8, the two g-C<sub>3</sub>N<sub>4</sub> show the same adsorption energy trend as A > B > C, owing to the strong interaction and proper space in zone A. A notable increase of adsorption energy can be observed after O atoms or hydroxyl groups introduced into CN skeleton. After protonation, the adsorption energy value becomes 3.0 times in zone A and 2.3 times in zone B as great. But no obvious difference is observed in zone C, ascribing to the same structure. The results confirm that the vacancies can provide adsorption active sites to activate N<sub>2</sub>. More detailed information for geometry optimizing and adsorption energy calculation are shown in Table S9.

Gibbs free energy in N<sub>2</sub> fixation over two g-C<sub>3</sub>N<sub>4</sub> samples was also investigated (Fig. 7b). More details about g-C<sub>3</sub>N<sub>4</sub> related geometry optimizing are shown in Fig. S10. Compared with pristine one, V-rich g-C<sub>3</sub>N<sub>4</sub> exhibits a lower Gibbs free energy in the whole process, suggesting its higher catalytic activity [29]. The first step of N<sub>2</sub> fixation reaction is the most difficult in the whole reaction procedure, exhibiting non-spontaneous adsorption behavior over both two g-C<sub>3</sub>N<sub>4</sub>. An obvious decrease of free energy can be found in the proton transfer reaction (from NNH to NHNH<sub>2</sub>) over V-rich g-C<sub>3</sub>N<sub>4</sub>. The reaction energies of these two steps for V-rich g-C<sub>3</sub>N<sub>4</sub> are calculated to be  $-0.82$  and  $-0.14$  eV while  $-0.93$  and  $-0.52$  eV in pristine g-C<sub>3</sub>N<sub>4</sub> respectively. However, few difference of energy occurs between these two g-C<sub>3</sub>N<sub>4</sub> in the last two reaction step, with the reaction energy of  $-0.53$  and

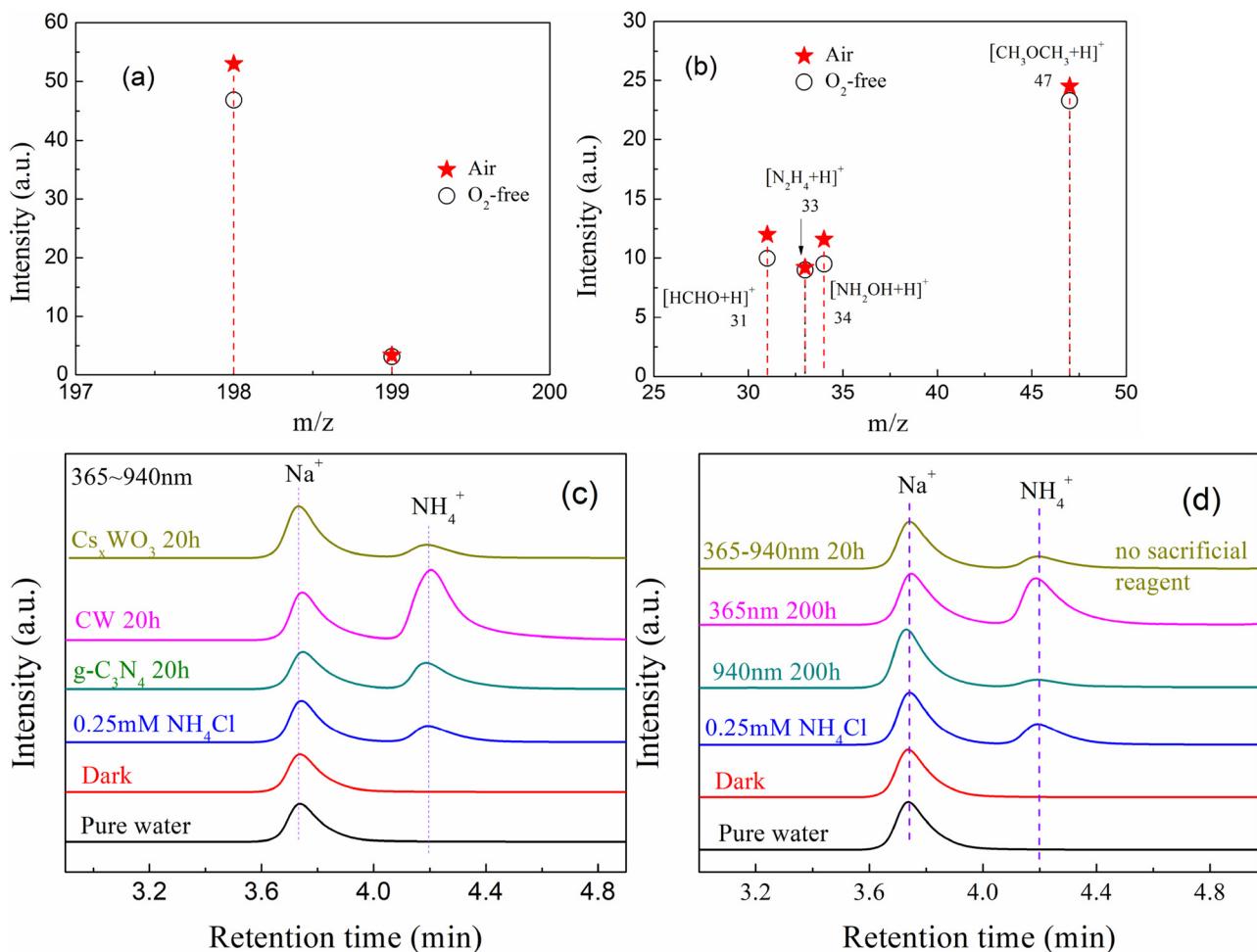


Fig. 5. Mass spectra of the (a) indophenol and (b) reaction solution over CW photocatalyst; Ion chromatography spectrum of reaction solution over (c) CW, g-C<sub>3</sub>N<sub>4</sub> and Cs<sub>x</sub>WO<sub>3</sub> photocatalyst under full spectrum light irradiation, and (d) CW photocatalyst.

–0.66 eV for pristine g-C<sub>3</sub>N<sub>4</sub> and –0.50 and –0.64 eV for V-rich one. The results reveal that V-rich g-C<sub>3</sub>N<sub>4</sub> exhibits better proton transfer ability as well as N<sub>2</sub> adsorption ability [19].

In addition, it is important to investigate the nitrogen source of NH<sub>3</sub> during N<sub>2</sub> fixation reaction over CW photocatalyst. First, N<sub>2</sub> fixation reaction was performed in the dark and N<sub>2</sub> atmosphere with different

temperature. As shown in Table 1, little NH<sub>3</sub> generation was observed. However, the production of NH<sub>3</sub> greatly increased in the room temperature under full spectrum light irradiation. It indicates the crucial importance of light irradiation and the certain thermal stability of CW photocatalyst. Second, the same reaction was carried out in Ar atmosphere under full spectrum light irradiation. The results show that the

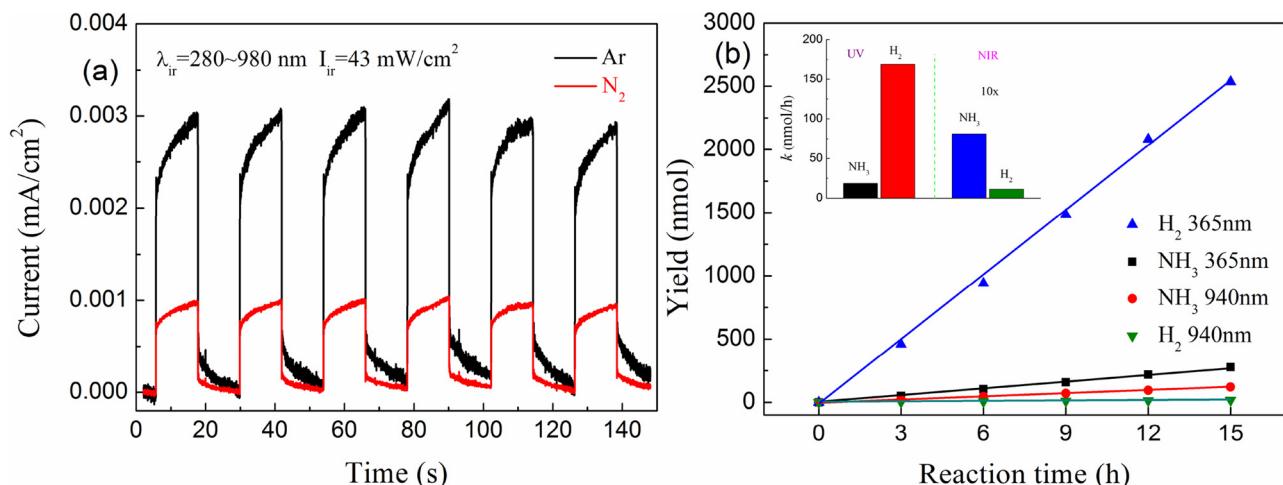
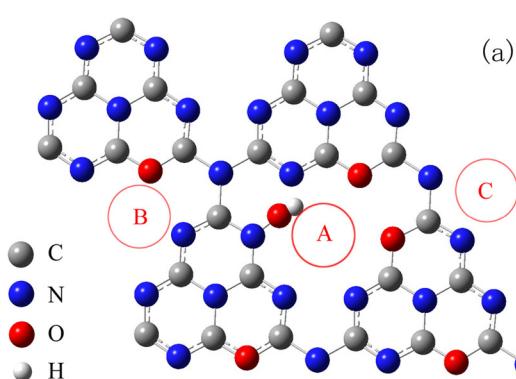


Fig. 6. (a) Photocurrent response under full spectrum light in Ar or N<sub>2</sub> gas and (b) Photoelectrochemical NH<sub>3</sub> and H<sub>2</sub> generation under 365 or 940 nm light irradiation over CW photoelectrode.



**Fig. 7.** Theoretical prediction of (a)  $\text{N}_2$  adsorption on V-rich  $\text{g-C}_3\text{N}_4$  at different zones and (b) Free energy change in the reaction procedure. (A)–(C): potential adsorption sites.

**Table 1**  
Photocatalytic  $\text{N}_2$  fixation over CW composite.

N <sub>2</sub> fixation			
Light (nm)	Temp. (K)	Air	NH <sub>3</sub> Yield (umol h <sup>-1</sup> g <sup>-1</sup> )
dark	293	N <sub>2</sub>	0.010
dark	313	N <sub>2</sub>	0.011
dark	333	N <sub>2</sub>	0.012
365–940	298	N <sub>2</sub>	331
365–940	298	Ar	3.2

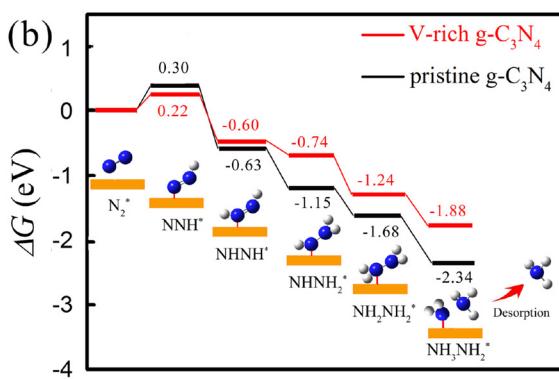
**Table 2**  
LC-MS analysis summary.

LC-MS		
Indophenol addition	m/z	peak
No	33	[N <sub>2</sub> H <sub>4</sub> + H] <sup>+</sup>
No	34	[NH <sub>2</sub> OH + H] <sup>+</sup>
Yes	198	<sup>14</sup> N-indophenol anion
Yes	199	<sup>15</sup> N-indophenol anion

**Table 3**  
Elemental content analysis.

Elemental content (%)	Fresh catalysts	Used catalysts
C	24.54	24.37
N	13.30	13.35
Cs	7.35	7.32
W	31.08	31.02
O	21.60	21.71
H	2.13	2.23

$\text{NH}_3$  generation rates are  $331 \mu\text{mol h}^{-1} \text{g}^{-1}$  in  $\text{N}_2$  atmosphere and  $3.2 \mu\text{mol h}^{-1} \text{g}^{-1}$  in Ar. The huge difference of  $\text{NH}_3$  production between the presence and absence of  $\text{N}_2$  atmosphere confirms that  $\text{N}_2$  is the nitrogen source of  $\text{NH}_3$ . In addition, LC-MS measurement was also performed to monitor the production of  $\text{N}_2$  fixation reaction. The results of Fig. 5 were summarized in Table 2. As mentioned before, no impurity  $m/z$  peaks were observed in the LC-MS analysis, indicating the stability of CW in the photocatalytic  $\text{N}_2$  fixation. It is worth mentioning that the existence of <sup>15</sup>N<sub>2</sub> signal further illustrates the  $\text{N}_2$  gas is the nitrogen source. In addition, to further study the stability of CW photocatalyst, the elemental analysis was also employed before and after ten times repeated  $\text{N}_2$  fixation reactions over CW. As shown in Table 3, no obvious differences can be observed between the fresh and used CW in the elemental analysis. The slight increase in the content of N, H and O could be caused by the absorption of  $\text{NH}_3$  or other oxide species on the



surface. Therefore, no nitrogen left the CW photocatalyst to form  $\text{NH}_3$  in the  $\text{N}_2$  fixation.

#### 4. Conclusion

In summary, we demonstrate that atmospheric  $\text{N}_2$  can be efficiently reduced to  $\text{NH}_3$  by  $\text{g-C}_3\text{N}_4/\text{Cs}_x\text{WO}_3$  composite under full-spectrum light, without any precious metal cocatalysts. Along with the visible light activity of  $\text{g-C}_3\text{N}_4$  and the NIR light absorption of  $\text{Cs}_x\text{WO}_3$ , the designed vacancies could activate  $\text{N}_2$  and significantly promote the interfacial electron transfer. The  $\text{N}_2$  fixation rate of CW in this study was high in different light irradiation and selectivity towards  $\text{NH}_3$  over  $\text{H}_2$  is realized by using NIR light. UV-NIR light synergistic effect can improve the photocatalytic  $\text{N}_2$  fixation largely. Above all, with the proper control of methanol,  $\text{O}_2$  plays a positive role in ammonia synthesis. It is like that a good horse always needs a good spur. With the protection of a sacrificial agent, the produced  $\text{NH}_3$  will not be oxidized. However, excess sacrificial agent will expend excessive amount of active species, then it does not have enough species to prepare ammonia. A proper sacrificial agent is very important. Since  $\text{O}_2$  and sacrificial agent are common presence, the present finding of their relationship in formation of the final product as a promoter might be stimulating for other catalytic reactions.

#### Acknowledgements

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.04.081>.

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